



Electrolyte features and microstructure affecting the electrochemical performance of a Pb–Sb alloy for lead-acid battery components

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ABSTRACT

The aim of this paper is to develop a comparative experimental study on the electrochemical features of a Pb–1 wt% Sb casting alloy in two different sulfuric acid solutions at room temperature. A water-cooled unidirectional solidification system was used to obtain alloy samples having different microstructural characteristics. These samples were subjected to tests in two different sulfuric acid (H₂SO₄) solutions: 0.5 M and 5.0 M H₂SO₄ and the resulting electrochemical impedance spectroscopy (EIS) plots, potentiodynamic polarization curves and an equivalent circuit analysis were used to evaluate the corresponding electrochemical behaviour. The experimental current density was found to be similar for all the examined Pb–Sb samples, and decreased with the increase in the cellular spacing, independently of the concentration of sulfuric acid in the solution. However, the EIS parameters demonstrated to be more affected by the scale of the cellular array in a 5 M H₂SO₄ solution. Nevertheless, it is shown that Pb–Sb alloys having coarse cell spacings have higher potential for application as grid material in lead-acid batteries.

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1. Introduction

A number of Pb alloys have been improved and developed in order to be applied in the production of positive and negative grids, connectors, posts and straps components of lead-acid batteries [1–5]. Considering the rapid development on lead-acid battery components for automotive applications in the past few decades, the lead-acid manufacturers have great concerns about the mechanical and corrosion resistance of these components, which must resist the stresses of the charge/discharge reactions without bending, stretching or warping, besides other aspects such as achieving a maintenance-free condition, lower water consumption, deterioration at high temperatures, and concentration of the electrolyte [5–9]. Lead acid battery manufacturers have introduced modifications to the grid project, on alloys composition, on the manufacturing processes (including the control of solidification variables) [5–13].

A constructional aspect of a lead-acid battery which considerably can affect the discharge and charge cycles and its performance and durability, is the specific resistance of the electrolyte and its freezing point, and as direct consequence, the sulfuric acid con-

centration. The electrolyte can be considered as an active material that participates in the cell reactions of a lead-acid battery [14]. Pavlov et al. [14] have demonstrated that the life-cycle of batteries decreases with the increase in acid concentration. A number of other studies have also evidenced the detrimental effect of higher acid concentrations on the life-cycle of lead-acid batteries considering both negative and positive grids [14–19]. Pavlov et al. [17] have extensively investigated the correlation between the influence of sulfuric acid (H₂SO₄) concentration on the electrochemical activity of the lead oxide (PbO₂) active mass and on the capacity and life-cycle performance of lead-acid batteries. They concluded that the charge efficiency can be improved when the specified charge voltage is lower than 14 V, and the acid concentration is lower than 1.24 g cm^{−3} (of about 5.0 mol L^{−1} or 5.0 M) which allows a complete charge and avoids reversible sulfation [14]. On the other hand, when the sulfuric acid concentration is higher than 1.24 g cm^{−3}, as is the case of VRLA batteries, higher initial capacity is demanded and as a consequence the corresponding performance is associated with a shorter life-cycle. They have also suggested that the performance of a VRLA battery may substantially be improved if H₂SO₄ concentrations lower than 1.24 g cm^{−3} were employed [14]. It is also important to remark that in the investigation developed by Pavlov and collaborators, it was also shown that the lead sulfate solubility depends strongly on the sulfuric acid concentration [14,17,19]. PbO₂ also depended on the pH of the synthesis electrolyte [19]. It

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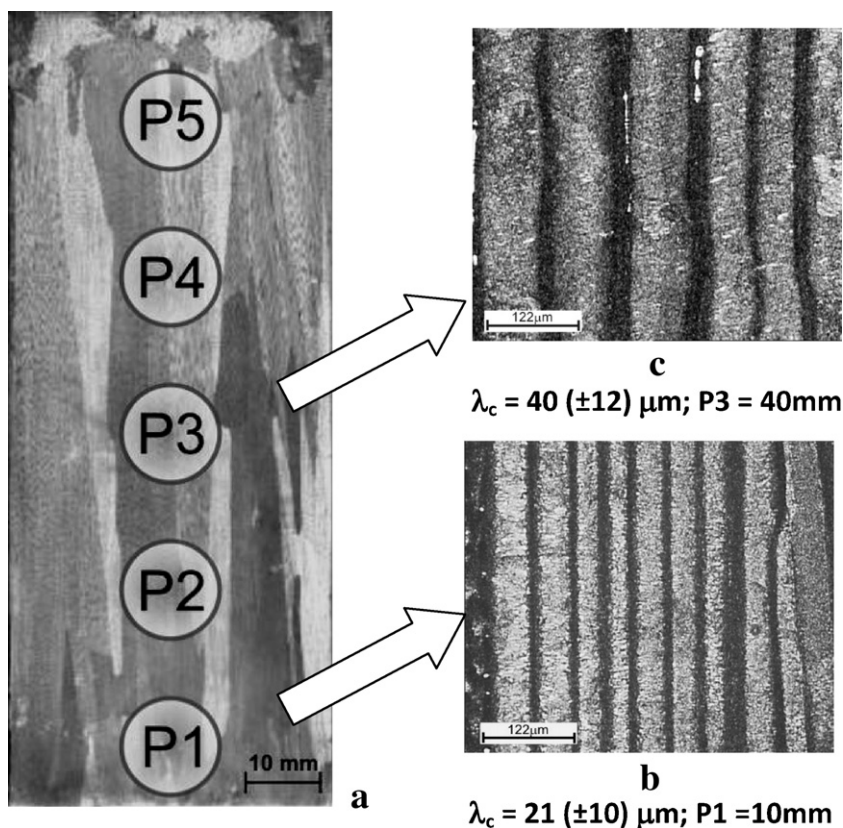


Fig. 1. (a) Typical unidirectional columnar macrostructure; micrograph of (b) fine and (c) coarse cellular spacings of a Pb–1 wt.% Sb alloy casting. *P* is the distance from the cooled bottom of the casting.

is well known that the solution characteristics, such as the pH and the temperature may also affect the corrosion mechanism and the corrosion behaviour of metallic alloys [20–22].

Considering the metallurgical features of dilute Pb alloys used in the manufacture of battery components, it has been reported [23–29] that coarse cellular arrays are associated with better corrosion resistance than fine ones in a 0.5 M H₂SO₄ solution. Although different studies focusing on metallurgical or constructional aspects of Pb alloys grids in the search for improvements in lead-acid batteries performance can be found in the literature [5–13,23–29], the present study aims to contribute with an analysis of the combined effects of metallurgical features and the sulfuric acid concentration of the electrolyte solution on the alloy electrochemical behaviour. A Pb–1 wt.% Sb alloy and 0.5 mol L^{−1} (of about 1.03 g cm^{−3}) and 5.0 mol L^{−1} (of about 1.28 g cm^{−3}) H₂SO₄ solutions at 25 °C are used in the experimental study.

2. Experimental procedure

2.1. Specimens preparation

Pb–1 wt.% Sb alloy samples were prepared by using commercially pure metals: Pb (99.89; ±0.02 wt.%) and Sb (99.8; ±0.02 wt.%). The main impurities were: Fe (0.053, ±0.01%), Si (0.018; ±0.01%), and Cu (0.012; ±0.01%), besides other minor elements with concentration less than 100 ppm.

A water-cooled unidirectional solidification setup, which was designed in such way that the heat is extracted only through a water-cooled bottom promoting vertical upward directional solidification, was used in the experiments. More details concerning the directional casting assembly can be found in previous articles [23–29]. Pb–Sb alloy samples were sectioned from the center of the casting, ground, polished and etched to reveal the macrostructure

using 80 cm³ of HNO₃ in 220 cm³ of distilled water and 45 g of ammonium molybdate (NH₄)₂MoO₄ in 300 cm³ of distilled water [23–29]. The microstructure was revealed by using a 37 cm³ glacial acetic acid and 15 cm³ of hydrogen peroxide solution at room temperature [23–29].

2.2. Electrochemical corrosion tests

Electrochemical impedance spectroscopy (EIS) tests were performed by using a 1 (±0.02) cm² circular area of ground (1200 grit SiC finish) sample surfaces, immersed in stagnant and naturally aerated 500 cm³ of two different sulfuric acid concentrations: (1) a 0.5 M H₂SO₄ solution (of about 1.03 g cm^{−3}) at 25 °C with a pH of 0.92 (±0.04) and (2) a 5.0 M H₂SO₄ solution (of about 1.28 g cm^{−3}) at 25 °C with a pH of 0.89 (±0.05), used to simulate the battery electrolyte. The measurements began after an initial delay of 30 min for the samples to reach a steady-state condition. The potential amplitude was set to 10 mV in open-circuit, peak-to-peak (AC signal), with 5 points per decade and the frequency range was set from 100 mHz to 100 kHz.

The samples for corrosion tests were collected at a midway position along the casting length considering specific distances (P1 and P3) from the bottom of the casting, as depicted in Fig. 1. These samples were further ground to a 1200 grit SiC finish, followed by distilled water washing and air drying before measurements.

Potentiodynamic measurements were also carried out in the aforementioned solution at 25 °C using a potentiostat at the same positions where the EIS tests were carried out. The potentiodynamic polarization curves were plotted using an automatic data acquisition system, and the corrosion rate and the corrosion potential were estimated by Tafel plots using both anodic and cathodic branches at a scan rate of 0.2 mV s^{−1} from −250/+250 mV (SCE) in open-circuit. Duplicate tests for EIS and potentiodynamic polariza-

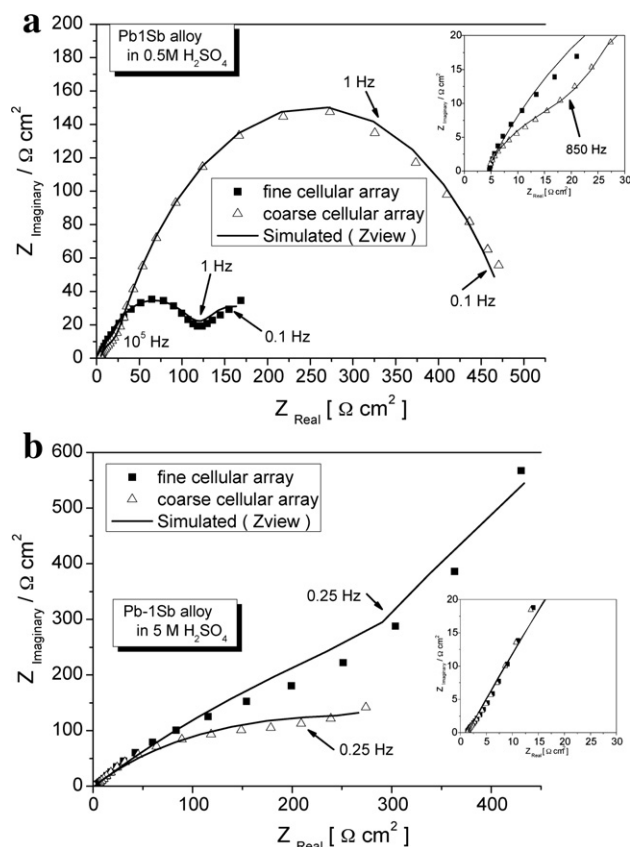


Fig. 2. Experimental and simulated Nyquist results for fine and coarse cellular spacings of the Pb–1 wt.% Sb alloy in: (a) 0.5 M H_2SO_4 and (b) 5.0 M H_2SO_4 solutions at room temperature.

tion curves were carried out. In order to supply quantitative support for discussions of these experimental EIS results, an appropriate model (ZView version 2.1b) for equivalent circuit quantification was used.

3. Results and discussion

3.1. Macrostructures and microstructures

Due to the water-cooled unidirectional system, the growth of columnar grains has prevailed along the entire casting length, as shown in Fig. 1. The samples for corrosion tests were collected at a midway position along the casting length as shown in a schematic representation in Fig. 1. Typical microstructures observed along longitudinal sections of Pb–1 wt.% Sb alloy castings are shown in Fig. 1(b). The microstructure consists of a completely cellular array, formed by a Pb-rich matrix (α -phase: solid solution of antimony in lead) with a eutectic mixture in the intercellular regions. The Pb-rich matrix is represented by white regions with the intercellular region depicted by dark regions. The water-cooled mold imposes higher values of cooling rates near the casting/chill surface (bottom) and a decreasing profile along the casting length (toward the top of the casting) due to the increase in the thermal resistance of the solidified shell with distance from the cooled surface [23–29].

3.2. Results of the EIS tests

3.2.1. Electrolyte: 0.5 M H_2SO_4 solution

Fig. 2 shows the experimental and simulated (Zview®) Nyquist plots of the Pb–Sb alloy samples examined in both 0.5 and 5.0 M H_2SO_4 solutions at 25 °C. A complete capacitive arc is observed for

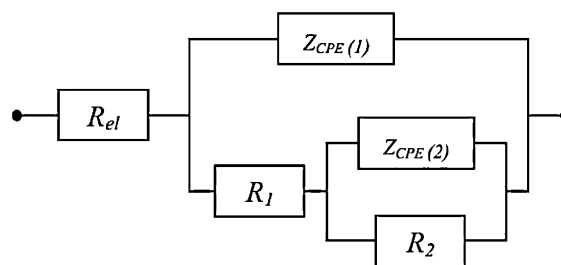


Fig. 3. Proposed equivalent circuit used to obtain impedance parameters.

the coarse cellular array with frequencies from 10^5 Hz up to 0.1 Hz. On the other hand, a capacitive arc at high frequencies (between 10^5 Hz and 1 Hz) followed by a slope of about 45° for frequencies lower than 1 Hz can be observed associated with the fine cellular array, as shown in Fig. 2(a). These Nyquist plots reveal that the diameter of the capacitive arc for the coarse array is higher than that of the fine one when examined in a 0.5 M H_2SO_4 solution at room temperature. These results indicate that the coarse array sample has better electrochemical behaviour than that of the fine cellular sample. At frequencies between 10^5 and 10^4 Hz (low Z_{Real} and $Z_{\text{Imaginary}}$), corresponding to about 5–30 $\Omega \text{ cm}^2$ (in Z_{Real}), different reactions between either the electrolyte and the surfaces of the samples or the electrolyte and complex products of corrosion on the surfaces of the coarse and fine arrays can be detected. The coarse array sample tends to depict a small capacitive semi-arc corresponding to $Z_{\text{Imaginary}} = 10 \Omega \text{ cm}^2$ and $Z_{\text{Real}} = 20 \Omega \text{ cm}^2$ at 850 Hz, as observed in Fig. 2(a). It seems that reactions between the electrolyte and pure lead oxidizing in various forms of lead sulfate (e.g. $\text{XPbO} \cdot \text{PbSO}_4$) [19] are associated with this capacitive semi-arc.

3.2.2. Solution: 5.0 M H_2SO_4 solution

Considering the concentrated sulfuric acid solution, the results are characterized by capacitive arcs at high frequencies (between 10^5 Hz and 0.25 Hz) followed by slight trends to slopes of about 45° at frequencies lower than 0.25 Hz, as shown in Fig. 2(b). A considerable higher capacitive arc for the fine cellular array sample is observed when compared with that of the coarse array sample. At frequencies between 10^5 and 10^4 Hz, corresponding to 5 to about 30 $\Omega \text{ cm}^2$ (Z_{Real}), similar reactions between the electrolyte and the surfaces are evidenced. These results suggest that more concentrated sulfuric acid solutions favor the development of high capacitive arcs, making easier the formation of oxide films or complex lead oxides. However, a quantitative analysis comparing EIS parameters between the coarse and fine arrays performed in both 0.5 and 5.0 M H_2SO_4 solutions would be necessary in order to permit a reliable conclusion on the resulting electrochemical response of these as-cast Pb–Sb alloy samples to be attained.

3.3. Impedance parameters and equivalent circuit analysis

An equivalent circuit analysis has also been conducted in order to obtain some impedance parameters, as demonstrated in Fig. 3. The impedance parameters obtained by the ZView® software, are shown in Table 1. The fitting quality was evaluated by chi-squared (χ^2) values of 7.5×10^{-3} and 8.5×10^{-3} and 5.4×10^{-4} and 41×10^{-4} for the Pb–1 wt.% Sb alloy in 0.5 M and 5.0 M H_2SO_4 solutions, respectively.

The interpretation of the physical elements of the proposed equivalent circuit is similar to those reported in previous studies [22–29]. R_{el} is the electrolyte resistance, R_1 is the charge transfer resistance and R_2 stands for a polarization resistance due to the participation of adsorbed intermediates. $Z_{\text{CPE}(1)}$ and $Z_{\text{CPE}(2)}$ denote the double layer capacitance and the capacitance associated with

Table 1

Impedance parameters for both fine and coarse cellular arrays of Pb–1 wt.% Sb alloy samples in 0.5 M and 5.0 M H₂SO₄ solutions at room temperature.

Parameters	Fine cell array $\lambda_c = 21 (\pm 10) \mu\text{m}$	Coarse cell array $\lambda_c = 80 (\pm 12) \mu\text{m}$
Solution: 0.5 M H ₂ SO ₄		
$R_{el} (\Omega \text{ cm}^2)$	4.2	4.1
$Z_{CPE(1)} (\mu\text{F cm}^{-2})$	309 (± 3.5)	157 (± 6)
$Z_{CPE(2)} (10^{-3} \times \text{F cm}^{-2})$	17.2 (± 2.5)	0.23 (± 0.03)
n_1	0.65	0.65
n_2	0.76	0.75
$R_1 (\Omega \text{ cm}^2)$	123 (± 8)	30 (± 0.8)
$R_2 (\Omega \text{ cm}^2)$	81 (± 12)	465 (± 3)
χ^2	41×10^{-4}	5.4×10^{-4}
Parameters	Fine cell array	Coarse cell array
Solution: 5 M H ₂ SO ₄		
$R_{el} (\Omega \text{ cm}^2)$	1.34	1.38
$Z_{CPE(1)} (\mu\text{F cm}^{-2})$	1516 (± 0.7)	1802 (± 0.6)
$Z_{CPE(2)} (10^{-3} \times \text{F cm}^{-2})$	0.85 (± 0.2)	22 (± 2.2)
n_1	0.60	0.62
n_2	0.99	0.99
$R_1 (\Omega \text{ cm}^2)$	2185 (± 889)	469 (± 51)
$R_2 (\Omega \text{ cm}^2)$	$6.7 \times 10^{13} (\pm 1.3 \times 10^{10})$	$6.7 \times 10^{13} (\pm 8.5 \times 10^9)$
χ^2	8.5×10^{-3}	7.5×10^{-3}

the polarization resistance R_2 . The parameters n_1 and n_2 are correlated to the phase angle, varying between -1 and 1 . The impedance of a constant phase element is defined as $Z_{CPE} = [C(j\omega)^n]^{-1}$ [22–29], where C is the capacitance; j is the current; ω is the frequency and $-1 \leq n \leq 1$. The value of n seems to be also associated with the non-uniform distribution of current as a result of roughness and surface defects [22–29].

It can be seen that both $Z_{CPE(1)}$ and $Z_{CPE(2)}$ of the coarse cell array sample are lower than those of the fine cell array sample and associated with higher R_2 , which favors the electrochemical response of the coarse sample when comparing the impedance parameters obtained in a 0.5 M H₂SO₄ solution. It is also important to remark that R_1 and R_2 can also represent the resistances of the porous (outer) and inner barrier (more compact) layers, respectively [30–35], which are associated to the charge transfer resistance through the porous layer and the participation of adsorbed intermediates [30–35]. In this sense, the higher R_2 inner layer resistance of the coarse sample evidences a better general electrochemical behaviour when compared with that of the fine cell array sample. The coarse cell sample exhibits a R_1 (porous layer) of about $30 \Omega \text{ cm}^2$ which agrees with the previous observations concerning the semi-arc at 850 Hz (low Z_{Real} and $Z_{\text{Imaginary}}$). R_1 of about $123 \Omega \text{ cm}^2$ for the fine cell array sample associated with a lower R_2 (barrier layer) than that of the coarse one, indicates that the fine cell structure is more susceptible to the corrosion action with higher production of outer porous layer when compared with the coarse sample. The higher R_2 value observed for the coarse cell array indicates a more compact product of corrosion.

Considering the impedance parameters obtained in a 5.0 M H₂SO₄ solution, it can be seen that the resistance of the electrolyte (R_{el}) decreased of about four times when compared with that corresponding to the more dilute solution, as shown in Table 1. It can also be clearly observed higher R_2 for both coarse and fine cell arrays when compared with R_1 , which indicates that the barrier (inner) layer is more compact than those observed for samples examined in a 0.5 M H₂SO₄ solution. This is an indication that R_2 has an important role on the electrochemical response of Pb–Sb alloys [30–35]. On the other hand, a higher R_1 value observed for the fine structure reveals that this cellular array has a greater susceptibility to the formation of an outer porous layer than the coarse one.

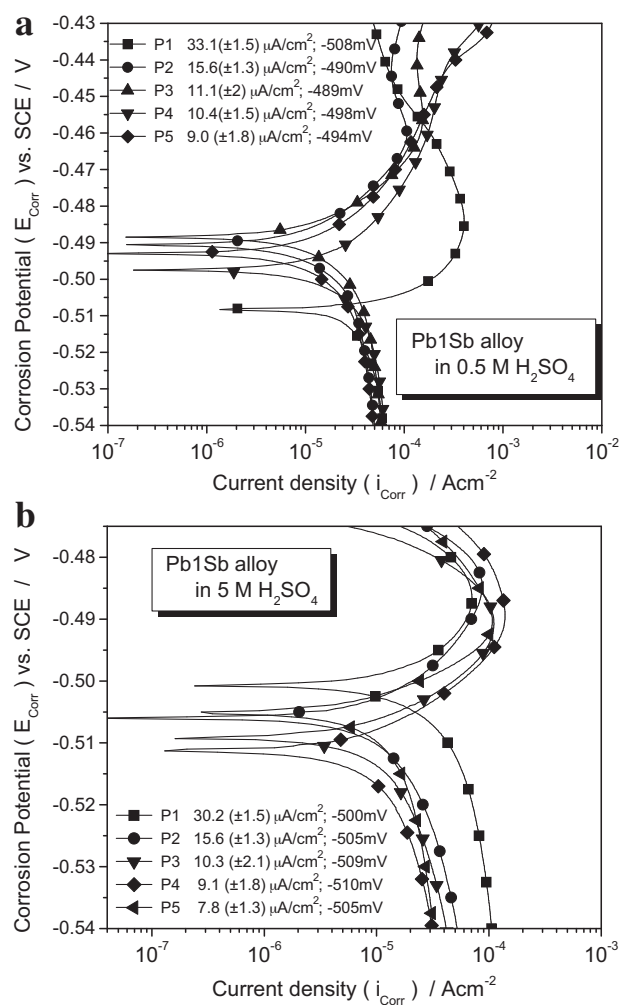


Fig. 4. Experimental potentiodynamic polarization curves for the fine and coarse cellular arrays of the Pb–1 wt.% Sb alloy in: (a) 0.5 M H₂SO₄ and (b) 5.0 M H₂SO₄ solutions at room temperature.

3.4. Polarization curve measurements

Fig. 4 shows potentiodynamic polarization curves (from -0.54 to -0.43 V and from -0.54 to -0.47 V vs. SCE) for the Pb–1 wt.% Sb alloy samples in both 0.5 M H₂SO₄ and 5.0 M H₂SO₄ solutions at 25 °C. The corrosion current density (i_{corr}) was obtained from Tafel plots using both the cathodic and anodic branches of the polarization curves. Although the experimental polarization curves of the Pb–1 wt.% Sb alloy samples carried out in 0.5 M and 5 M H₂SO₄ solutions indicate similar corrosion potentials, i.e. between -0.49 V and -0.51 V (SCE) and -0.50 and -0.51 V (SCE), respectively, the shapes of the corresponding curves are reasonably different, mainly displacing the potential from -0.49 V (SCE) toward the nobler potential side with the increase in the cellular spacing.

At potentials between -0.52 and -0.49 V (SCE), it can be said that anodic oxidation of Pb to Pb (II) ions is started. However, it is important to remember that the rate of anodic oxidation of Pb to Pb (II) ions at potentials about -0.45 V (SCE) is not the process that determines the corrosion rate of lead in sulfuric acid. Associated with this aforementioned range of potentials some amounts of lead sulfate (PbSO₄) crystals can be formed and reduced (dissolution-precipitation mechanism) due to the high solubility of PbSO₄ in the 0.5 M H₂SO₄ solution. Above a potential of about -0.08 V (SCE), selected Pb²⁺ can be formed or reduced along with some hydro-

gen and/or oxygen evolution and lead oxide (PbO) can be formed [26–29,36–38].

The present experimental results have shown that coarser cells tend to improve the corrosion resistance of a Pb–1 wt.% Sb alloy mainly due to the reduction in cellular boundaries, as previously reported for Pb–Sn alloys [26–29]. The cell boundaries are regions of higher energy which is a result of distortions at the limits between adjacent cells during growth along the solidification process. These results show that the resulting microstructural morphology has an important role on the electrochemical behaviour of the Pb–Sb alloy examined.

Fig. 5 shows the experimental results of current density and corrosion potential of the Pb–1 wt.% Sb alloy samples in both 0.5 M and 5.0 M H_2SO_4 solutions at room temperature as a function of the cellular spacing. It can be seen in Fig. 5(a) that the current density is similar for a given cellular spacing independently of the electrolyte concentration, and that it decreases with the increase in the cellular spacing. Typical micrographs of cellular arrays at three different positions along the casting are also depicted in Fig. 5(a).

When a 0.5 M H_2SO_4 solution is considered, a trend showing a slight increase in the corrosion potential (characterized by a displacement toward the nobler-side) with the increase in the cellular array can be observed. On the other hand, the corrosion potential is displaced toward a more active potential when a 5.0 M H_2SO_4 solution is considered, as shown in Fig. 5(b).

Despite the experimental results of EIS (impedance parameters) and of the potentiodynamic polarization curves, it can be concluded that: (i) in a 0.5 M H_2SO_4 solution at 25 °C, both EIS and polarization results evidence that coarser cellular structures tend to yield higher corrosion resistance than finer cellular arrays. This behaviour is intimately associated with the reduction in cellular boundaries when compared with finer cells, since the boundary has proved to be more susceptible to the corrosion action, as also previously reported [24–29] and (ii) in a 5.0 M H_2SO_4 solution at 25 °C, the analysis of the EIS parameters indicates that both fine and coarse cells delineate a similar inner oxide layer (R_2 of about $7 \times 10^{13} \Omega \text{ cm}^2$), as shown in Table 1. However, the fine cell array has a higher charge transfer resistance ($R_1 = 2 \text{ k}\Omega \text{ cm}^2$) than the coarse one ($R_1 = 460 \Omega \text{ cm}^2$), which corresponds to an outer oxide layer (porous layer) which is thicker and rougher than that of the coarse array. This observation associated with the R_2 measurements (inner and more compact oxide layer) indicates that the fine structure has a greater susceptibility to the corrosion action when tested in a more concentrated sulfuric acid solution.

It is important to remark that the sulfuric acid concentration changes the kinetics of formation of corrosion products (such as PbSO_4 , its variation $\text{XPbO} \cdot \text{PbSO}_4$, and evolution for PbO and PbO_2 when higher potentials are considered) [19] and can also signifi-

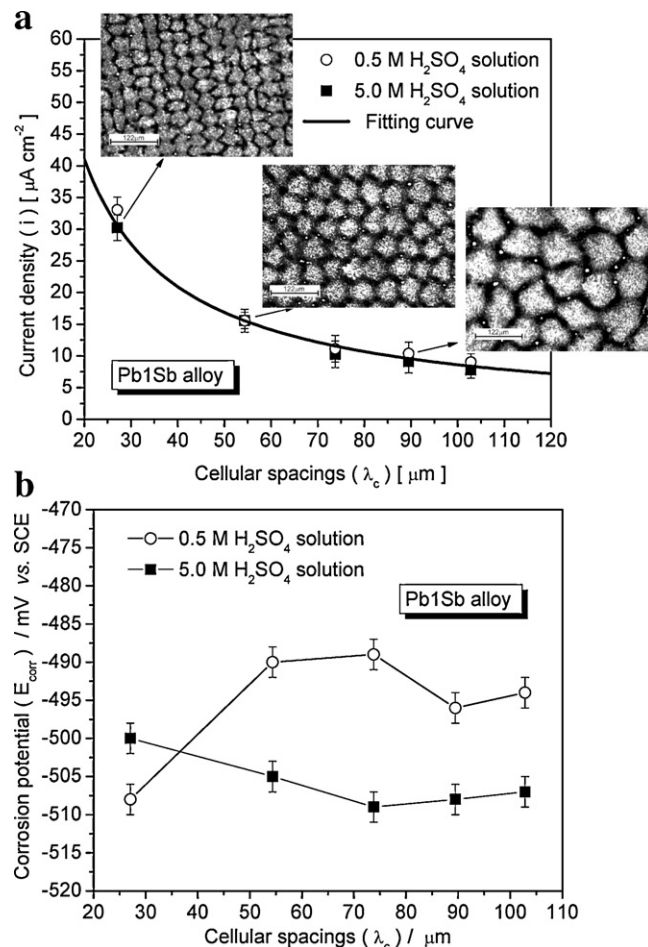


Fig. 5. (a) Experimental current density and (b) corrosion potential of the Pb–1 wt.% Sb alloy in both 0.5 M and 5.0 M H_2SO_4 solutions at room temperature as a function of the cellular spacing.

cantly affect the charge/discharge mechanism of lead acid batteries, and consequently modifies the battery life-time cycle. Despite the experimental evidence of properties of outer and inner layers and on the nature and rate of the oxidation processes at the surface of the samples, there are indications that the cellular arrangement controls the corrosion evolution. Fig. 6 demonstrates similar corrosion products (oxide layer) at the surfaces of both coarse and fine cellular samples.

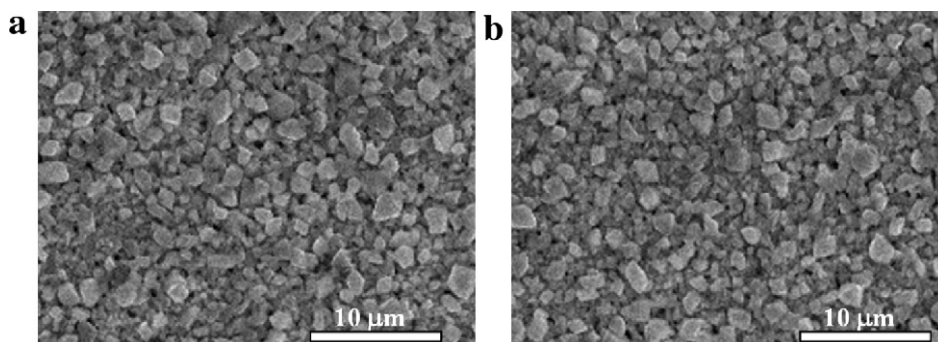


Fig. 6. Typical SEM images of a Pb–1 wt.% Sb alloy sample: (a) fine and (b) coarse cell arrays resulting in Pb oxide layers on the surface of the samples after polarization tests in a 0.5 M H_2SO_4 solution.

4. Conclusions

The present experimental electrochemical parameters have shown that Pb–1 wt.% Sb alloy samples having a coarse cellular array have higher corrosion resistance if compared with samples characterized by fine cellular arrays. It was found that, for a given cell spacing, the current density in both 0.5 M and 5.0 M H₂SO₄ solutions at room temperature is similar. It was also shown that independently of the considered sulfuric acid concentration, the current density for all examined Pb–Sb samples decreased with the increase in the cell spacing. This demonstrates that the cell spacing associated with the intercellular boundaries (active regions) will determine the corrosion susceptibility of as-cast dilute Pb–Sb alloys, since the cell boundaries are regions of higher energy and distortions at the limits between adjacent cells (which occur during solidification). The EIS experimental parameters obtained by the ZView[®] software have also supported the aforementioned findings. It can be said that independently of the concentration of the sulfuric acid solution, a coarse cellular array provides better electrochemical behaviour than fine ones. In this sense, the control of solidification processing variables (e.g. cooling rate) of dilute Pb–Sb alloys can be considered by the manufacturers of as-cast components as an alternative way to produce lead-acid battery components with better electrochemical behaviour.

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